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Activator-Free Palladium-Catalyzed Silylation of Aryl Chlorides with Silylsilatranes

Yutaro Yamamoto,[a] Hiroshi Matsubara,*[b] Kei Murakami,[a,c] Hideki Yorimitsu,*[a,d] and Atsuhiro Osuka[a]

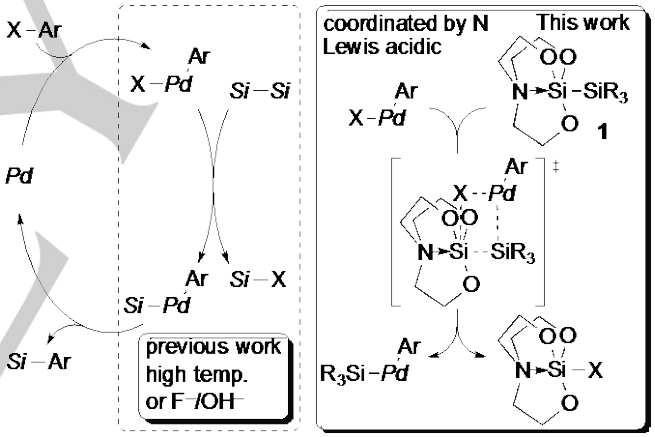
Dedication ((optional))

Abstract: Palladium-catalyzed silylation of aryl chlorides with silylsilatranes **1** proceeds under activator-free conditions, hence displaying wide functional group compatibility to allow boryl and siloxy groups to survive. Experimental and computational studies have revealed that smooth transmetalation from silylsilatranes to arylpalladium chloride is facilitated by strong interaction between the Lewis acidic silicon and the chloride.

Introduction

Due to the important roles that organosilicon compounds play in organic chemistry, chemists have devoted much time to develop new efficient reactions for carbon–silicon bond formation.[1] Since the conventional nucleophilic attack of chlorosilanes with organomagnesium or -lithium reagents suffers from functional group compatibility,[2] silylation under milder conditions have been drawing significant attention.[1a,3–12] Among them, transition-metal-catalyzed silylation of aryl halides with disilanes represents an attractive tool (Scheme 1, left).[4–6,11,12] However, the silylation with disilane generally requires very high temperatures such as 140–170 ˚C[4] or highly basic reaction conditions.[6] Milder protocols for achieving efficient silylation with wider functional group compatibility are therefore highly sought after.

Palladium-catalyzed silylation with disilane consists of oxidative addition of aryl halide to palladium(0), transmetalation between arylpalladium halide and disilane, and reductive elimination. Taking the low reactivity of disilanes into consideration, one should focus on the transmetalation step to achieve activator-free mild silylation.[5,13] To this end, we designed unsymmetrical disilane, silylsilatrane **1** (Scheme 1, right). We initially envisioned that internal coordination of the nitrogen atom should facilitate Si–Si bond cleavage for facile transmetalation.[14–16] Indeed, in the literature, arylstannatranes and -germatranes are known to be more reactive in activator-free cross-coupling reactions than the corresponding trialkyl analogs.[15] We also expected that the silatrane moiety of **1** would be still more Lewis acidic than a triorganosilyl group to realize efficient interaction with halide on palladium for both smooth transmetalation and selective transfer of the triorganosilyl group of **1**.



Scheme 1. Catalytic Cycle for Pd-catalyzed Silylation with Disilane and Our Design of Silylsilatrane **1**.

Results and Discussion

Synthesis of **1** was easy and scalable (See Experimental Section). For instance, nucleophilic substitution reaction of readily available ethoxysilatrane with dimethylphenylsilyllithium afforded dimethylphenylsilylsilatrane (**1a**) on a 12-g scale (Figure 1). Silylsilatranes **1** are fairly stable and can be stored in air for more than one year without detectable decomposition. Therefore, silylsilatranes **1** have a practical advantage over the corresponding simpler trialkoxydisilanes such as R_3Si–$Si(OMe)_3$.[17] X-ray crystallographic analysis of **1a** (Figure 1) revealed that the length of the Si–Si bond (2.3426(9) Å) is close to that of a typical symmetrical disilane (2.354(2) Å for $(FpCH_2)Me_2Si$–$SiMe_2(CH_2Fp)$ (Fp = $(\eta^5$-$C_5H_5)Fe(CO)_2)$).[18] This similarity indicates that the transannular coordination of the nitrogen atom to the bridgehead silicon is not so effective as to

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elongate the Si–Si bond despite a short transannular N–Si distance of 2.153(2) Å.

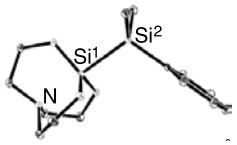


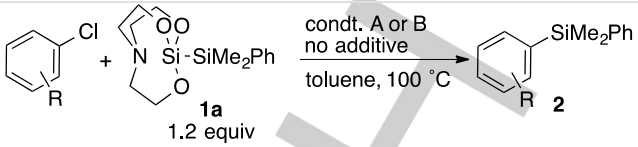
Figure 1. Synthesis and ORTEP Drawing of Silylsilatrane **1a**. Thermal ellipsoids represent 50% probability.

With silylsilatrane **1** in hand, we examined silylation of aryl halides under palladium catalysis. To our delight, the reaction of electron-rich aryl chloride with **1a** proved to proceed at 100 ˚C under $Pd_2(dba)_3$/SPhos[19] catalysis in the absence of an additive (Table 1, entries 1–5). As we expected, the dimethylphenylsilyl group of **1a** was selectively transferred and none of arylsilatranes were detected. Under the fluoride-free conditions, a siloxy group was naturally compatible (entry 2). Arylsilane **2d** bearing a substituent at the *ortho* position was obtained in good yield after 30 h (entry 4). Unfortunately, the $Pd_2(dba)_3$/SPhos catalysis did not work for the reaction of electron-deficient aryl chlorides (entry 7). After rescreening of catalysts, $Pd(PtBu_3)_2$[20,21] showed an excellent catalytic activity in converting electron-deficient aryl chlorides (entries 8–11). Notably, the chloro group of 4-chlorophenylboronate was substituted with the silyl group with the boronate moiety intact (entry 12). Both catalytic systems are effective in silylating electronically neutral chlorotoluenes (entries 6, 13, and 14).

The scope of silylsilatrane **1** was surveyed (Table 2). Bulkier silyl groups were transferred efficiently (entries 1 and 2). Trimethylsilylsilatrane (**1d**) was less reactive yet participated in the silylation with the aid of RuPhos[19] at a higher temperature in DMF. The silatrane skeleton of **1** is important for efficient silyl transfer: simple hexaorganodisilane and monoalkoxydisilane reacted sluggishly (entries 4 and 5).

Surprisingly, attempts to silylate aryl bromide and triflate failed and resulted in the recovery of the starting material under the standard conditions (Scheme 2, eq 1).[22] Considering that oxidative addition of aryl bromide and triflate should be much easier than that of aryl chloride, we speculated that the transmetalation step would be problematic and that chloride on palladium would play a crucial role in smooth transmetalation. Indeed, lithium chloride as an additive promoted the silylation (eqs 2 and 3), probably through halide ligand exchange between arylpalladium bromide or triflate and lithium chloride. We confirmed this ligand exchange process by ^{31}P NMR analysis (See Supporting Information).

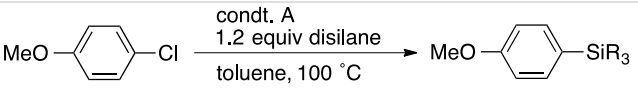
Table 1. Silylation of Aryl Chlorides with Silylsilatrane **1a**

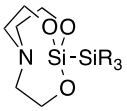


entry	R	Condt.[a]	2	Yield [%]
1	4-MeO	A	**2a**	89
2	4-TBDMSO	A	**2b**	91
3[b]	4-AcHN	A	**2c**	78
4[c]	2-MeO	A	**2d**	71
5[d]	(3-chlorothiophene)	A	**2e**	74
6	4-CH_3	A	**2f**	77
7	4-CF_3	A	**2g**	0[g]
8	4-CF_3	B	**2g**	99
9	4-CO_2Et	B	**2h**	96
10	3-CN	B	**2i**	96
11[e]	3-NO_2	B	**2j**	71
12[f]	4-Bpin	B	**2k**	69
13[f]	3-CH_3	B	**2l**	71
14	4-CH_3	B	**2f**	77

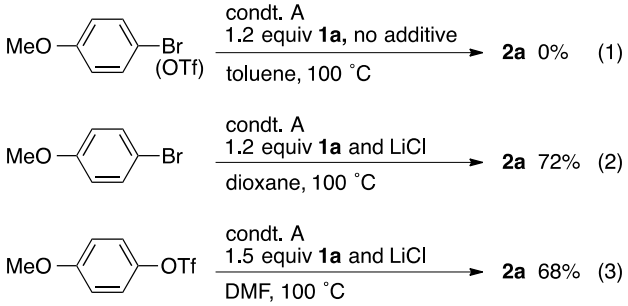
[a] condt. A: 3 mol % Pd_2dba_3, 9 mol % SPhos, 12 h; condt. B: 5 mol % $Pd(PtBu_3)_2$, 10 h. [b] 1.0 equiv **1a**. [c] 30 h. [d] 8 h. [e] 40 h. [f] 10 mol % catalyst. [g] >90% recovery of the starting material.

Table 2. Scope of Disilane



entry	Disilane		Product	Yield [%]
1		$SiMePh_2$ (**1b**)	**3**	81
2[a]		$SiMe_2$(*o*-tolyl) (**1c**)	**4**	90
3[b]		$SiMe_3$ (**1d**)	**5**	54 (74[c])
4	$Me_2PhSi-SiMe_2Ph$		**2a**	11
5	(*i*PrO)$Me_2Si-SiMe_2Ph$		**2a**	16

[a] 5 mol % $Pd_2(dba)_3$ and 15 mol % SPhos. [b] RuPhos was used instead of SPhos. Performed in DMF at 120 ˚C. [c] NMR yield.



Scheme 2. Silylation of Aryl Bromide and Triflate.

To investigate the effect of the chloride ligand in the smooth transmetalation, DFT calculations were performed by using Gaussian 09.[23,24] We chose transmetalation between PhPdX(P*t*Bu$_3$) and trimethylsilylsilatrane (**1d**) as a model reaction for computational simplicity (Figure 2). Transmetalation between PhPdCl(P*t*Bu$_3$) and **1d** was calculated to proceed via a four-membered transition state **TS_Cl** in a concerted manner with an activation barrier of 98.7 kJmol^{-1}. The transmetalation results in formation of **Prod_Cl**, in which the chloride weakly coordinates to palladium. The overall reaction is slightly endothermic by 14.7 kJmol^{-1}. On the other hand, the activation energy for transmetalation between PhPdBr(P*t*Bu$_3$) and **1d** was calculated to be 114.1 kJmol^{-1} and **TS_Br** is more difficult to reach by 15.4 kJmol^{-1} than **TS_Cl**. The formation of product **Prod_Br** is significantly endothermic (44.2 kJmol^{-1}), which correlates with late transition state **TS_Br** with the higher activation energy. These results show that the efficient silylation of aryl chloride is based on intrinsically strong interaction between silicon and chlorine in the transmetalation.[25,26]

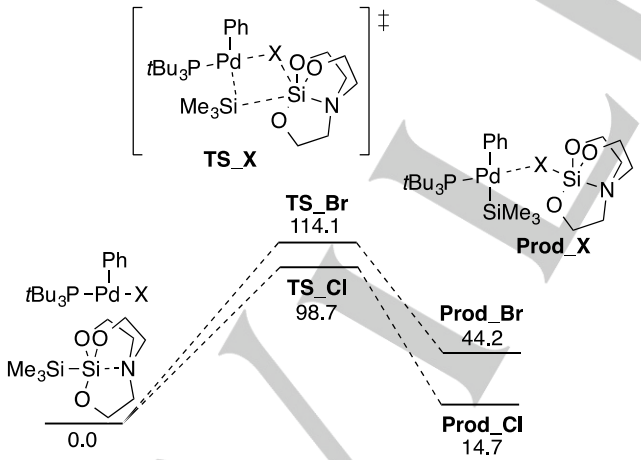


Figure 2. Energy profile of transmetalation obtained by DFT calculations at the M06/6-311G**+ECP(Pd,P,Si,Cl,Br) level. Energies are in kJmol^{-1}.

Conclusions

We have developed silylsilatranes as promising silylating agents in palladium-catalyzed silylation of aryl chlorides under activator-free conditions. A variety of functional groups such as boryl and siloxy groups are tolerant due to the absence of a basic activator. Experimental and computational investigations have revealed that the success of the activator-free silylation relies on smooth transmetalation between arylpalladium chloride and silylsilatranes, which takes advantage of the affinity between the chloride on the palladium and the Lewis acidic silicon. These findings contain important information about still unexplained transmetalation in general, and have significant impacts on development of new activator-free reactions of moderately reactive organometalloid reagents of low toxicity, which are underway in our laboratory to realize ultimate activator-free cross-coupling reactions.

Experimental Section

^{1}H NMR (600 MHz), ^{13}C NMR (151 MHz), ^{31}P NMR (243 MHz), and ^{29}Si NMR (119 MHz) spectra were taken on a JEOL ECA-600 spectrometer. Chemical shifts were reported as delta scale in ppm relative to $CHCl_3$ (δ = 7.26) for ^{1}H NMR, to $CDCl_3$ (δ = 77.16) for ^{13}C NMR, to H_3PO_4 (δ = 0.00) for ^{31}P NMR, and to tetramethylsilane (δ = 0.00) for ^{29}Si NMR. Spectroscopic grade solvents were used for all spectroscopic studies without further purification. IR spectra were determined on a JASCO IR-810. High-resolution APCI-TOF mass spectra were taken on a Bruker microTOF. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel 60F$_{254}$. Preparative separations were performed by silica gel chromatography (Wako gel C-200, C-300, or C-400). Crystallographic data were collected on a Rigaku RAXIS–RAPID apparatus at –180 °C using graphite-monochromated Cu$K\alpha$ radiation (λ = 1.54187 Å). The structures were solved by direct method (SHELXS-97) and refined with full-matrix least square technique (SHELXL-97).[27]

Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Toluene, *N*,*N*-dimethylformamide (DMF), and hexamethylphosphoric triamide (HMPA) were distilled from CaH_2. Tris(dibenzylideneacetone)dipalladium ($Pd_2(dba)_3$), SPhos, RuPhos, and lithium wire were purchased from Sigma-Aldrich. Pd(P*t*Bu$_3$)$_2$ was purchased from Strem and was stored and weighed in a glove box filled with nitrogen. Anhydrous THF was purchased from Wako Pure Chemical Industries, Ltd. and stored under nitrogen.

Synthesis of Dimethylphenylsilylsilatrane (1a): Ethoxysilatrane[28] (14.6 g, 72 mmol) was placed in a reaction flask. The flask was purged with nitrogen, and THF (120 mL) was added. Dimethylphenylsilyllithium[29] (ca. 1.0 M solution in THF, 72 mL, 72 mmol) was added to the solution via a cannula. The reaction mixture was stirred at room temperature. After 20 min, the reaction was quenched with a saturated NH_4Cl solution and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo to afford white solids. The solids were suspended in hexane (10 mL) and the suspension was then filtered off. The solids were washed on the filter paper with hexane to afford **1a** (12.0 g, 38.9 mmol, 54%). Colorless solid. Mp 164–165 °C. IR (neat): 1425, 1109, 1072, 936, 807, 757, 733, 698, 617 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.66–7.63 (m, 2H), 7.31–7.23 (m, 3H), 3.75 (t, *J* = 5.5 Hz, 6H), 2.78 (t, *J* = 5.5 Hz, 6H), and 0.52 (s, 6H); ^{13}C NMR ($CDCl_3$) δ (ppm): 142.80, 134.58, 127.68, 127.35, 58.10, 51.42, and –1.80; ^{29}Si NMR ($CDCl_3$, 60 °C) δ

(ppm): –25.70 and –66.96; APCI-TOF-MS: *m/z* = 309.1202. calcd for $C_{14}H_{23}NO_3Si_2$: 309.1211 $[M]^+$. Crystal data for **1a**: $C_{14}H_{23}NO_3Si_2$, from CCl_4/EtOH, *M* = 309.51, Monoclinic, $P2_1/n$ (No. 14), *a* = 6.613(2), *b* = 21.9028(4), *c* = 10.7275(2) Å, β = 94.0357(17)°, *V* = 1561.27(6) Å^3, *Z* = 4, *T* = 93 K, ρ_{calcd} = 1.317 g/cm^3, R_1 = 0.0573 ($I > 2.0\ \sigma(I)$), wR_2 = 0.1547 (all data), GOF = 1.142, CCDC No.: 985696.

Synthesis of Methyldiphenylsilylsilatrane (1b): Ethoxysilatrane (2.44 g, 12 mmol) was placed in a reaction flask. The flask was purged with nitrogen, and THF (20 mL) was added into the flask. Methyldiphenylsilyllithium[30] (ca. 1.0 M solution in THF, 18 mL, 18 mmol) was added to the solution via a cannula. The reaction mixture was stirred at room temperature. After 20 min, the reaction was quenched with a saturated NH_4Cl solution and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo to afford white solids. The solids were suspended in hexane (5 mL) and the suspension was then filtered off. The solids were washed on the filter paper with hexane to afford **1b** (1.02 g, 2.75 mmol, 23%). Colorless solid. Mp 170–171 °C. IR (neat): 1427, 1271, 1108, 1067, 910, 748, 735, 700, 629 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.71–7.66 (m, 4H), 7.32–7.27 (m, 6H), 3.77 (t, *J* = 5.5 Hz, 6H), 2.76 (t, *J* = 5.5 Hz, 6H), and 0.57 (s, 3H); ^{13}C NMR ($CDCl_3$) δ (ppm): 140.91, 135.47, 127.83, 127.35, 57.95, 51.33, and –2.87; ^{29}Si NMR ($CDCl_3$, 60 °C) δ (ppm): –26.56 and –69.02; APCI-TOF-MS: *m/z* = 371.1360. calcd for $C_{19}H_{25}NO_3Si_2$: 371.1367 $[M]^+$. Crystal data for **1b**: $C_{19}H_{25}NO_3Si_2$, from 1,2-Dichloroethane/EtOH, *M* = 371.58, Orthorhombic, *P*bca (No. 61), *a* = 11.4397(3), *b* = 24.7612(6), *c* = 13.1386(3) Å, *V* = 3721.65(16) Å^3, *Z* = 8, *T* = 93 K, ρ_{calcd} = 1.326 g/cm^3, R_1 = 0.0516 ($I > 2.0\ \sigma(I)$), wR_2 = 0.1183 (all data), GOF = 1.077, CCDC No.: 985697.

Synthesis of Dimethyl(*o*-tolyl)silylsilatrane (1c): Et_2O (15 mL) and dichlorodimethylsilane (60 mmol, 9.0 mL) were added to a reaction flask purged with nitrogen. The reaction mixture was cooled to 0 °C. 2-Methylphenylmagnesium bromide (0.62 M in THF, 81 mL, 50 mmol) was added to the solution at 0 °C via a cannula, which was warmed to room temperature. After the reaction mixture was stirred overnight, the resulting suspension was filtered off and washed on the filter with hexane to collect the filtrate. After evaporation of the solvent, chlorodimethyl(*o*-tolyl)silane was distilled under reduced pressure (3 torr, 78 °C, 5.37 g, 29.0 mmol, 58%). Lithium wire (500 mg, 70 mmol) in oil was cut into 4-mm cubes with scissors. These lithium cubes were stirred vigorously for 10 min in hexane (5 mL) under nitrogen. The hexane was removed and the lithium was suspended in THF (15 mL). The mixture was stirred rapidly with chlorodimethyl(*o*-tolyl)silane (3.0 mL, 18 mmol) at room temperature for 6 h to give a deep red solution of Me_2(*o*-tolyl)SiLi (ca. 1.0 M). Ethoxysilatrane (2.44 g, 12 mmol) was placed in a reaction flask. The reaction flask was purged with nitrogen, and THF (20 mL) was added into the reaction flask. Dimethyl(*o*-tolyl)silyllithium (ca. 1.0 M solution in THF, 18 mL, 18 mmol) was added to the solution via a cannula. The reaction mixture was stirred at room temperature. After 30 min, the reaction was quenched with a saturated NH_4Cl solution and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo to afford white solids. The solids were suspended in hexane (5 mL) and the suspension was then filtered off. The solids were washed on the filter paper with hexane to afford **1c** (486 mg, 1.50 mmol, 13%). Colorless solid. Mp 143–144 °C. IR (neat): 1453, 1274, 1110, 1075, 874, 812, 740, 624, 588 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.56 (d, *J* = 6.4 Hz, 1H), 7.17 (t, *J* = 7.8 Hz, 1H), 7.13–7.07 (m, 2H), 3.72 (t, *J* = 5.5 Hz, 6H), 2.76 (t, *J* = 5.5 Hz, 6H), 2.52 (s, 3H), and 0.35 (s, 6H); ^{13}C NMR ($CDCl_3$) δ (ppm): 144.52, 140.72, 135.21, 129.29, 128.11, 124.58, 58.32, 51.57, 23.35, and –1.06; ^{29}Si NMR ($CDCl_3$, 60 °C) δ (ppm): –25.62 and –65.51; APCI-TOF-MS: *m/z* = 323.1352. calcd for $C_{15}H_{25}NO_3Si_2$: 323.1367 $[M]^+$.

Synthesis of Trimethylsilylsilatrane (1d): Ethoxysilatrane (6.58 g, 30 mmol) and THF (40 mL) were added to a reaction flask under nitrogen. Trimethylsilyllithium[31] (ca. 0.24 M in THF, 62 mL, 15 mmol) was added to the solution via a cannula. The reaction mixture was stirred overnight at room temperature. The reaction was quenched with a saturated NH_4Cl solution and extracted with EtOAc. The organic layer was washed with brine, dried over anhydrous Na_2SO_4, filtered, and concentrated to afford white solids. The solids were suspended in hexane (5 mL) and were then filtered off. The solids were washed on the filter paper with hexane to afford **1d** (1.04 g, 4.2 mmol, 28%). Colorless solid. Mp 171–174 °C. IR (neat): 1110, 1077, 935, 849, 824, 744, 726, 640, 613 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ (ppm): 3.73 (t, *J* = 5.5 Hz, 6H), 2.76 (t, *J* = 5.5 Hz, 6H), and 0.04 (s, 9H); ^{13}C NMR ($CDCl_3$) δ (ppm): 58.29, 51.47, and –0.81; ^{29}Si NMR ($CDCl_3$, 60 °C) δ (ppm): –23.85 and –64.03; APCI-TOF-MS: *m/z* = 247.1061. calcd for $C_9H_{21}NO_3Si_2$: 247.1054 $[M]^-$.

Synthesis of 1,1,2,2-Tetramethyl-1-phenyl-2-isopropoxydisilane: Ether (100 mL) and 1,2-dichloro-1,1,2,2-tetramethyldisilane (30 mmol, 5.56 mL) were added to a reaction flask purged with nitrogen. The reaction mixture was cooled to 0 °C. PhMgBr (0.47 M in Et_2O, 60 mL, 28.2 mmol) was added. After stirring at 0 °C for 8 h, the resulting suspension was filtered off and washed on the filter with hexane to collect the filtrate. After evaporation, 1-chloro-2-phenyl-1,1,2,2-tetramethyldisilane was distilled under reduced pressure (3 torr, 89 °C, 4.29 g, 18.7 mmol, 62%). DMAP (2.5 mmol, 305.4 mg), imidazole (6.0 mmol, 408.5 mg), and 1-chloro-2-phenyl-1,1,2,2-tetramethyldisilane (5.0 mmol, 1.14 mL) were placed in a reaction flask. The reaction flask was purged with nitrogen, and DMF (25 mL) was added. The reaction mixture was cooled to 0 °C, and *i*PrOH (10 mmol, 0.77 mmol) was added dropwise. The reaction mixture was stirred at room temperature for 3 h and was then quenched by addition of water. The reaction mixture was diluted with ether. The layers were separated, and the aqueous layer was extracted with ether. The organic extracts were washed with brine three times, dried over anhydrous Na_2SO_4, filtered, and concentrated in vacuo to afford a colorless liquid. The product was distilled under reduced pressure (2 torr, 73–74 °C, 757 mg, 3.0 mmol, 60%). Colorless liquid. IR (neat): 1244, 1120, 1106, 1018, 876, 825, 786, 763, 731, 679, 633 cm^{-1}. ^{1}H NMR ($CDCl_3$) δ (ppm): 7.53–7.48 (m, 2H), 7.37–7.30 (m, 3H), 3.87 (septet, *J* = 5.9 Hz, 1H), 1.09 (d, *J* = 5.9 Hz, 6H), 0.39 (s, 6H), and 0.23 (s, 6H); ^{13}C NMR ($CDCl_3$) δ (ppm): 139.40, 134.04, 128.59, 127.92, 66.05, 25.96, 0.26, and –3.34; ^{29}Si NMR ($CDCl_3$, 60 °C) δ (ppm): 10.65 and –25.08; APCI-TOF-MS: *m/z* = 251.1270. calcd for $C_{13}H_{24}OSi_2$: 251.1282 $[M]^-$.

Typical Procedure for Silylation of Electron-Rich and Neutral Aryl Chlorides: The reaction of **1a** with 4-chloroanisole (Table 1, entry 1) is representative. $Pd_2(dba)_3$ (0.015 mmol, 13.7 mg) and SPhos (0.045 mmol, 18.5 mg) were added to a reaction flask. The reaction flask was purged with argon, and toluene (0.5 mL) was added. The reaction mixture was then stirred at room temperature for 10 min. 4-Chloroanisole (0.50 mmol, 71.2 mg) was added to the reaction flask and then the reaction mixture was stirred at room temperature for 5 min. Dimethylphenylsilylsilatrane (0.60 mmol, 185.7 mg) and toluene (1.0 mL) were added. The reaction mixture was then stirred at 100 °C for 12 h. The resulting mixture was diluted with AcOEt and passed through an alumina short column with copious washings with AcOEt. Chromatographic purification on silica gel by using AcOEt / hexane (1 / 40) as an eluent afforded **2a** (108 mg, 0.444 mmol) in 89% yield.

Typical Procedure for Silylation of Electron-Deficient and Neutral Aryl Chlorides: The reaction of **1a** with 1-chloro-4-trifluoromethylbenzene (Table 1, entry 8) is representative. Under inert atmosphere, Pd(P*t*Bu$_3$)$_2$ (0.025 mmol, 12.8 mg) was added to a reaction flask. Toluene (1.0 mL) and 1-chloro-4-trifluoromethyltoluene (0.50 mmol,

90.9 mg) were added to the reaction flask, and then the reaction mixture was stirred at room temperature for 5 min. Dimethylphenylsilylsilatrane (0.60 mmol, 185.7 mg) was added, and the reaction mixture was then stirred at 100 °C for 10 h. The resulting mixture was diluted with AcOEt and passed through a short alumina column with copious washings with AcOEt. Chromatographic purification on silica gel by using hexane as an eluent afforded **2g** (140 mg, 0.499 mmol) in 99% yield.

Products **2a**[32], **2d**[33], **2f**[34], **2g**[32], **2h**[32], **2l**[32], **3**[33], **4**[35], and **5**[36] are known compounds and showed the identical spectra according to the literature.

(4-*tert*-Butyldimethylsiloxyphenyl)dimethylphenylsilane (2b): Colorless oil. IR (neat): 1591, 1500, 1428, 1253, 1175, 1109, 911, 802, 774, 699, 653 cm^{-1}. ^1H NMR ($CDCl_3$) δ (ppm): 7.53–7.48 (m, 2H), 7.39–7.31 (m, 5H), 6.83 (d, J = 8.3 Hz, 2H), 0.98 (s, 9H), 0.52 (s, 6H), and 0.20 (s, 6H); ^{13}C NMR ($CDCl_3$) δ (ppm): 156.84, 138.92, 135.76, 134.30, 129.74, 129.11, 127.90, 119.79, 25.83, 18.34, –2.01, and –4.20; ^{29}Si NMR ($CDCl_3$, room temperature) δ (ppm): 20.62 and –8.45; APCI-TOF-MS: m/z = 343.1899. calcd for $C_{20}H_{31}OSi_2$: 343.1908 $[M + H]^+$.

(4-Acetylaminophenyl)dimethylphenylsilane (2c): Colorless solid. Mp 115–116 °C. IR (neat): 1669, 1590, 1530, 1371, 1322, 1292, 1247, 1112, 806, 778, 728, 701 cm^{-1}. ^1H NMR ($CDCl_3$) δ (ppm): 7.59–7.44 (m, 7H), 7.39–7.32 (m, 3H), 2.17 (s, 3H), and 0.54 (s, 6H); ^{13}C NMR ($CDCl_3$) δ (ppm): 168.67, 138.85, 138.35, 135.13, 134.25, 133.80, 129.22, 127.93, 119.31, 24.73, and –2.23; ^{29}Si NMR ($CDCl_3$, room temperature) δ (ppm): –8.25; APCI-TOF-MS: m/z = 270.1316. calcd for $C_{16}H_{20}NOSi$: 270.1309 $[M + H]^+$.

Dimethylphenyl(3-thienyl)silane (2e): Colorless oil. IR (neat): 1248, 1105, 821, 795, 769, 730, 697, 655, 607 cm^{-1}. ^1H NMR ($CDCl_3$) δ (ppm): 7.58–7.51 (m, 2H), 7.50–7.47 (m, 1H), 7.43–7.34 (m, 4H), 7.21 (d, J = 4.6 Hz, 1H), and 0.57 (s, 6H); ^{13}C NMR ($CDCl_3$) δ (ppm): 139.07, 138.50, 134.08, 132.98, 132.05, 129.30, 127.98, 125.94, and –1.64; ^{29}Si NMR ($CDCl_3$, 60 °C) δ (ppm): –12.42; APCI-TOF-MS: m/z = 217.0492. calcd for $C_{12}H_{14}SSi$: 217.0502 $[M - H]^-$.

(3-Cyanophenyl)dimethylphenylsilane (2i): Colorless oil. IR (neat): 2227, 1428, 1391, 1250, 1111, 850, 829, 793, 774, 733, 701 cm^{-1}. ^1H NMR ($CDCl_3$) δ (ppm): 7.78 (s, 1H), 7.74–7.71 (m, 1H), 7.66–7.62 (m, 1H), 7.53–7.49 (m, 2H), 7.47–7.37 (m, 4H), and 0.59 (s, 6H); ^{13}C NMR ($CDCl_3$) δ (ppm): 140.86, 138.32, 137.77, 136.53, 134.20, 132.58, 129.79, 128.48, 128.23, 119.28, 112.29, and –2.57; ^{29}Si NMR ($CDCl_3$, room temperature) δ (ppm): –7.08; APCI-TOF-MS: m/z = 238.1043. calcd for $C_{15}H_{16}NSi$: 238.1047 $[M + H]^+$.

Dimethyl(3-nitrophenyl)phenylsilane (2j): Colorless oil. IR (neat): 1522, 1346, 875, 833, 816, 778, 726, 700, 680, 662 cm^{-1}. ^1H NMR ($CDCl_3$) δ (ppm): 8.37 (s, 1H), 8.21 (d, J = 8.4 Hz, 1H), 7.81 (d, J = 7.3 Hz, 1H), 7.58-7.48 (m, 3H), 7.44-7.36 (m, 3H), and 0.64 (s, 6H); ^{13}C NMR ($CDCl_3$) δ (ppm): 148.00, 141.58, 140.30, 136.49, 134.19, 129.83, 128.92, 128.61, 128.25, 124.11, and –2.52; ^{29}Si NMR ($CDCl_3$, room temperature) δ (ppm): –6.75; APCI-TOF-MS: m/z = 258.0944. calcd for $C_{14}H_{16}NO_2Si$: 258.0945 $[M + H]^+$.

Dimethyl(4-pinacolatoborylphenyl)phenylsilane (2k): Colorless solid. Mp 87–94 °C. IR (neat): 1357, 1139, 1075, 808, 776, 746, 732, 700, 656 cm^{-1}. ^1H NMR ($CDCl_3$) δ (ppm): 7.79 (d, J = 7.8 Hz, 2H), 7.54 (d, J = 7.8 Hz, 2H), 7.52-7.49 (m, 2H), 7.38–7.31 (m, 3H), 1.35 (s, 12H), and 0.55 (s, 6H); ^{13}C NMR ($CDCl_3$) δ (ppm): 142.01, 138.20, 136.27, 134.32, 134.03, 133.62, 129.25, 127.94, 83.91, 24.99, and –2.34; ^{29}Si NMR ($CDCl_3$, room temperature) δ (ppm): –7.87; APCI-TOF-MS: m/z = 339.1960. calcd for $C_{20}H_{28}BO_2Si_2$: 339.1950 $[M + H]^+$.

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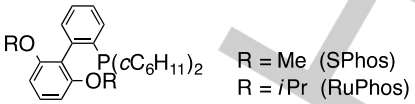

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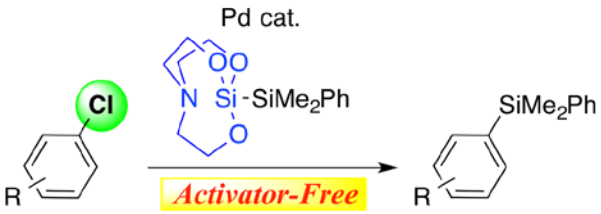

Palladium-catalyzed silylation of aryl chlorides with silylsilatranes proceeds under activator-free conditions, hence displaying wide functional group compatibility to allow boryl and siloxy groups to survive. Experimental and computational studies have revealed that the chloride on palladium plays important roles for smooth transmetalation from silylsilatranes to arylpalladium chloride is facilitated by strong interaction between the Lewis acidic silicon and the chloride.

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Activator-Free Palladium-Catalyzed Silylation of Aryl Chlorides with Silylsilatranes